

PATENT ABSTRACTS OF JAPAN

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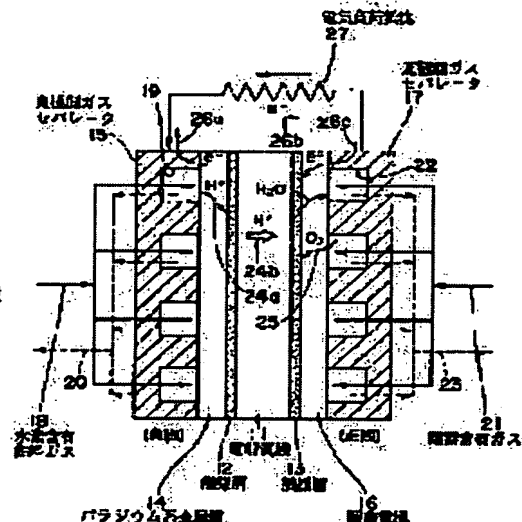
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(54) FUEL BATTERY

(57)Abstract:

PURPOSE: To provide a fuel battery to which a reformed gas can be directly supplied.

CONSTITUTION: In a fuel battery in which a gas 18 containing hydrogen is used as a fuel, a palladium series metal film 14 is provided as a hydrogen separation film of selectively transmitting hydrogen into the hydrogen pole side of a proton conduction type electrolyte layer 11. Hydrogen is preferentially transmitted from the gas touching the hydrogen pole through the palladium series metal film and transferred to the foregoing electrolyte layer to generate an electric power, so that a reformed gas can be supplied as a fuel direction to the battery without the gas containing hydrogen obtained by particularly reforming the fuel being refined with high purity in advance.



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CLAIMS

[Claim(s)]

[Claim 1] The fuel cell characterized by making hydrogen penetrate preferentially out of the gas which comes to arrange the hydrogen demarcation membrane which makes hydrogen penetrate alternatively to the hydrogen pole side of the electrolyte layer of a PURONTO conduction type in the fuel cell which operates considering the gas containing hydrogen as a fuel, and touches a hydrogen pole through the hydrogen demarcation membrane concerned, and generating electricity by transmitting to said electrolyte layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Without refining beforehand the hydrogen content gas which reforms especially the fuel concerned and is obtained to a high grade about the fuel cell which uses alcohol, such as hydrocarbons, such as methane, or a methanol, as a fuel, this invention is devised so that the hydrogen pole of the cell concerned can be directly supplied by using reformed gas as a fuel.

[0002]

[Description of the Prior Art] A fuel cell hardly generates the noise, when it is not necessary to use the fossil fuel which has the exhaustion problem of a resource, but since it has the description which was [make / compared with other energy engines / recovery effectiveness of energy / very high] excellent, it is use as a comparatively small power generating plant of a building unit or a works unit. In recent years, this fuel cell is used as a power source of the motor which replaces with the internal combustion engine for mount, and operates, and it considers driving a car etc. by this motor. In this case, it makes into a natural thing for an important thing to reuse the matter generated by the reaction as much as possible, and it is desirable for a not much big output to be small as much as possible with all the equipment of a not required thing, and the fuel cell which uses ion exchange membrane from such a point, especially the solid-state polyelectrolyte film fuel cell attract attention so that clearly also from it being an object for mount.

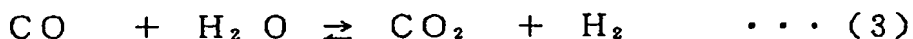
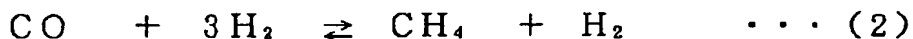
[0003] Here, the basic structure of the body of a solid-state polyelectrolyte film fuel cell is explained as an example, referring to drawing 4. As shown in this drawing, the cell proper 01 is constituted by joining gas diffusion electrodes 03A and 03B to the both sides of the solid-state polyelectrolyte film 02. And this zygote is manufactured by carrying out a hotpress etc., after setting gas diffusion electrodes 03A and 03B by the both sides of the solid-state polyelectrolyte film 02. Moreover, the reaction film 04A and 04B and the gaseous diffusion film 05A and 05B are joined, respectively, and, as for gas diffusion electrodes 03A and 03B, the front face of the reaction film 04A and 04B touches in the electrolyte membrane 02. Therefore, a cell reaction mainly occurs in the contact surface between an electrolyte membrane 02 and the reaction film 04A and 04B. moreover, the gas separator which has oxygen supply slot 06a in the front face of the above-mentioned gas diffusion electrode 03A -- moreover, the gas separator 07 which has hydrogen supply slot 07a is joined to the front face of gas diffusion electrode 03B of another side, respectively, and the oxygen pole and the hydrogen pole are constituted.

[0004] And if oxygen supply slot 06a and hydrogen supply slot 07a supply oxygen and hydrogen, respectively, oxygen and hydrogen will be supplied to the reaction film 04A and 04B side through each gaseous diffusion film 05A and 05B, and the following reactions will occur by the interface of each reaction film 04A and 04B and an electrolyte membrane 02.
interface [of reaction film 04A]: -- interface [of $O_2 + 4H^{++} + 4e^{-} \rightarrow 2H_2O$ reaction film 04B]: -- $2H_2 \rightarrow 4H^{++} + 4e^{-}$ here -- $4H^{+}$ Although it flows from a hydrogen pole to an oxygen pole through an electrolyte membrane 02, $4e^{-}$ will flow from a hydrogen pole to an oxygen pole through a load 08, and electrical energy is obtained.

[0005] By the way, when a hydrocarbon or alcohol is used as a raw material, as a conventional method of working a fuel cell and obtaining power, there is a thing as shown in drawing 3. In this drawing, after desulfurizing material gas first, if steam is mixed at a predetermined rate and it feeds into a reforming machine, the following steam-reforming reactions will advance under existence of a reforming catalyst. That is, if the example of methane shows, the reaction of following reaction-formula (1) - (3) shown in "*** 1" will advance.

[0006]

[Formula 1]



[0007] The reforming reaction of hydrocarbons, such as the above-mentioned methane, is H_2 , so that temperature is high, and a pressure is low from a viewpoint of thermodynamical equilibrium and there are many steam ratios. A reaction advances to the direction where the concentration of CO becomes high.

[0008] consequently, the outlet gas of a reforming machine -- H_2 others -- CH_4 , H_2O , and CO and CO_2 Although gas is contained, since CO serves as catalyst poison, generally with the fuel cell of a phosphoric acid mold or a solid-state polyelectrolyte membrane type, the reformed gas from a reforming machine cannot be used as fuel gas for direct fuel cells.

[0009] Then, reformed gas is fed into CO transformer and it is CO by the reaction (3) of the above-mentioned [bottom / of catalyst existence] H_2 It converts and mitigating CO concentration to about 0.5 - 1% is performed. When there is the need of furthermore reducing CO concentration, raising purity is performed until it applies the gas after CO conversion to a gas purifier further, for example, CO is set to 10 ppm or less. As a gas purification method at this time, there are means, such as low temperature processing, an adsorption separation method, the deoxo method by the palladium catalyst, a wet absorption purification method, and a diffusion method by the palladium system alloy film.

[0010] Thus, the heat of combustion of hydrogen is transformed to direct current power by supplying the gas (CO concentration having been reduced especially) containing the hydrogen of the high grade obtained to the hydrogen pole of a fuel cell, and supplying air or oxygen gas to another side and an oxygen pole.

[0011]

[Problem(s) to be Solved by the Invention] With the conventional technique which was mentioned above, it is a fuel cell, especially it is obliged to complicated down stream processing (refer to drawing 3) in especially concentration reduction of CO so that poisoning of the polar-zone catalytic-reaction layer may not be carried out.

[0012] That is, there are the following faults after a steam-reforming reaction.

1) Need CO transformer.

2) Need an altitude refiner further depending on the case.

3) Consequently, equipment expense and running cost become expensive and worsen economical efficiency.

[0013] This invention aims at offering the fuel cell which can supply reformed gas to the fuel cell concerned directly in view of the above-mentioned problem.

[0014]

[Means for Solving the Problem] The configuration of the fuel cell concerning this invention which attains said purpose is characterized by to make hydrogen penetrate preferentially out of the gas which comes to arrange the hydrogen demarcation membrane which makes hydrogen penetrate alternatively to the hydrogen pole side of the electrolyte layer of a PURONTO conduction type, and touches a hydrogen pole through the hydrogen demarcation membrane concerned, and to generate electricity by transmitting to said electrolyte layer in the fuel cell which operates considering the gas containing hydrogen as a fuel.

[0015] Hereafter, the contents of the fuel cell concerning this invention are explained to a detail.

[0016] It is the block diagram showing the outline of the fuel cell concerning this invention in drawing 1 . As shown in this drawing, while forming the catalyst bed 12 for hydrogen dissociation in one side face of an electrolyte membrane 11, the catalyst bed 13 for hydro-acid-izing is formed in the side face of another side. Moreover, the negative-electrode side gas separator 15 is laid on top of the palladium system metal membrane 14 list as a hydrogen demarcation membrane which serves as a hydrogen electrode in the side face of the catalyst bed 12 for one hydrogen dissociation one by one. The positive-electrode side gas separator 17 is laid on top of the oxygen electrode 16 list of porosity nature one by one also on the side face of the catalyst bed 13 for hydro-acid-izing of another side.

[0017] And the hydrogen content fuel gas 18 as reformed gas is discharged out of a system as a stream 20, after the fuel gas passage 19 formed in the above-mentioned negative-electrode side gas separator 15 is supplied and hydrogen is consumed in part. On the other hand, oxygen content gas 21, such as air, is discharged out of a system as a stream 23, after the oxygen content gas passageway 22 formed in the positive-electrode side gas separator 17 of the opposite side is supplied and oxygen is consumed in part.

[0018] The palladium system metal membrane 14 as a hydrogen demarcation membrane which serves as the above-mentioned hydrogen electrode here has the capacity to make only the hydrogen in hydrogen content fuel gas 18 penetrate alternatively, and it penetrates the inside of the palladium system metal membrane 14 concerned, and he is trying to lead the hydrogen of the above-mentioned hydrogen content fuel gas 18 to the electrolyte membrane 11 of a proton conduction type.

[0019] As a palladium system metal membrane 14 which makes this hydrogen penetrate alternatively, Pd single ****, the Pd-Ag alloy film, the Pd-Y alloy film, the Pd-Ag-Au-Ru alloy film, etc. can be mentioned, for example.

[0020] About passage of the hydrogen in these palladium system metal membranes, many researches are made after discovery of Graham, and the setup of the transparency device is as follows.

(1) A hydrogen content child sticks to the front face of the film by the side of raw gas.

(2) Dissociate to a hydrogen atom, with an adsorption hydrogen content child adsorbing.

(3) An adatom ionizes, separate into a proton and an electron and award an electron to a metal grid.

(4) It is spread in the opposite side (purification hydrogen side) from a membranous raw gas side in the state of a proton.

(5) A proton receives an electron from a metal grid in the opposite side, and the atom of the letter of adsorption generates.

(6) Association of two adsorption hydrogen atoms generates an adsorption hydrogen content child.

(7) a film surface to a hydrogen content child's desorption -- carry out.

Only the hydrogen which carries out a dissociative adsorption and can be in a proton condition by the above-mentioned step can carry out diffuse transmission of the inside of the film.

[0021] Next, the relation between the behavior of the hydrogen and the acid which are supplied as a fuel of the fuel cell which made the hydrogen pole the above-mentioned palladium system metal membrane 14, and the power to generate is explained below.

[0022] First, hydrogen infiltrates into said palladium system metal membrane 14 from the fuel gas passage 19 side by the side of a negative electrode, and by the alternative hydrogen permeation function of this film, after it moves to the other end of the palladium system metal membrane 14 concerned in the proton H+24a condition, it is diffused in the catalyst bed 12 for hydrogen dissociation in a hydrogen content child's condition. Next, by the catalysis of the catalyst bed 12 concerned, a hydrogen content child dissociates and is proton H+. Electron e - It generates. Furthermore, concerned proton H+ Proton H+ which diffuses an electrolyte membrane 11 O2 which is set to flow 24b, reaches the catalyst bed 13 for hydro-acid-izing, and diffuses the inside of the porous oxygen electrode 15 from the oxygen content gas-passageway 22 side by the side of a positive electrode It flows through flow 25 and an external electrical circuit. Electron e - Flow 26c is joined, it reacts and H2 O is generated. The H2 O concerned is the inside of an oxygen electrode 15 O2 In flow 25, it is spread in the reverse sense, and the positive-electrode side oxygen content gas passageway 20 is reached, and it is discharged.

[0023] That is, when the reaction in the polar zone is summarized, it comes to be shown in following "*** 2."

[0024]

[Formula 2]

In the catalyst bed 12 for hydrogen dissociation $H_2 \rightarrow 4H++4e- \dots$ (4)

In the catalyst bed 13 for hydro-acid-izing $4H++4e-+O_2 \rightarrow 2H_2 O \dots$ (5)

[0025] Electron e generated at the above-mentioned reaction (4) - Electron e - It becomes flow 26a, 26b, and 26c, moves to an antipole side, and contributes to a reaction (5). At this time, it is Electron e. - In case flow passes the electric load resistance 27, it will be outputted as power.

[0026] In the above-mentioned explanation, although the palladium system metal membrane 14 as a hydrogen demarcation membrane which makes the hydrogen prepared in the negative-electrode side penetrate alternatively is provided in one side face of the catalyst bed 12 for hydrogen demarcation membranes established in the side face of an electrolyte membrane 11 as shown in drawing 1 , it explains explanation of the fuel cell which it comes to constitute without using the catalyst bed 12 for these hydrogen demarcation membranes with reference to drawing 2 .

[0027] The configuration of the fuel cell shown in drawing 2 joins the palladium system metal membrane 14 to the side face of an electrolyte membrane 11 directly compared with the fuel cell shown in drawing 1 , and although the points which make unnecessary the catalyst 13 for hydrogen demarcation membranes differ, other configurations suppose that it is the same as that of the configuration of the fuel cell shown in drawing 1 . Therefore, about the overlapping member, the duplicate number is attached and the explanation is omitted.

[0028] Next, the relation between the behavior of the hydrogen and the acid which are supplied as a fuel of a fuel cell which makes a hydrogen pole the above-mentioned palladium system metal membrane 14, and it comes to join to the direct electrolyte membrane 11, and the power to generate is explained with reference to drawing 2 below.

[0029] Hydrogen infiltrates into said palladium system metal membrane 14 from the fuel gas passage 19 side by the side of a negative electrode. First, by the alternative hydrogen permeation function of this film After moving to the other end of the palladium system metal membrane 14 concerned in the proton H+24a condition, with the condition of proton H+24a -- the inside of the electrolyte membrane 11 concerned -- advancing -- further -- concerned proton H+ Proton H+ which diffuses an electrolyte membrane 11 O2 which is set to flow 24b, reaches the catalyst bed 13 for hydro-acid-izing, and diffuses the inside of the porous oxygen electrode 15 from the oxygen content gas-passageway 22 side by the side of a positive electrode It flows through flow 25 and an external electrical circuit. Electron e - Flow 26c is joined, it reacts and H2 O is generated. The H2 O concerned is the inside of an oxygen electrode 15 O2 In flow 25, it is spread in the reverse sense, and the positive-electrode side oxygen content gas passageway 20 is reached, and it is discharged.

[0030] That is, when the reaction in the polar zone is summarized, it comes to be shown in following "*** 3."

[0031]

[Formula 3]

In the front face (hydrogen pole side) of the palladium system metal membrane 14 which penetrates hydrogen alternatively H2 - >4H++4e- ... (6)

In the catalyst bed 13 for hydro-acid-izing 4H++4e-+O2 ->2H2 O ... (7)

[0032] Electron e generated at the above-mentioned reaction (6) - Electron e - It becomes flow 26a, 26b, and 26c, moves to an antipole side, and contributes to a reaction (7). At this time, it is Electron e. - In case flow passes the electric load resistance 27, it will be outputted as power.

[0033] For the above and the palladium system metal membrane 14, there is an operation which makes hydrogen ionize [ionize and it adsorption-dissociates / operation], and hydrogen is the inside of the film Proton H+ It moves in the condition. Therefore, it is proton H+ at joining the palladium system metal membrane 14 and an electrolyte membrane 11 directly. Flow can be delivered to an electrolyte membrane 11 from the palladium system metal membrane 14.

[0034]

[Example] Hereafter, based on the following examples, it explains that the fuel cell by this invention is effective. an electrical-potential-difference x current characteristic (IV property) -- 0.75Vx0.2 A/cm2 namely, power flux density -- 0.15 W/cm2 When operating a cell, it asks for the flux of the hydrogen which flows a cell. Since the hydrogen initial complements of per 1W are about 0.025 mols / h-w, using potential efficiency of a cell as 64%, it is power-flux-density 0.15 W/cm2. The hydrogen flux phiH2 at the time serves as a mol (0.15 (0.025)) / cm2 and h= 1.37cm3 / cm2, and mm. Below, the conditions of the palladium system metal membrane for obtaining the aforementioned hydrogen flux are examined. Hydrogen flux phiH2 which lets the palladium system metal membrane concerned pass It is given by the formula shown in-one following "number."

[0035]

[Equation 1]

$$\phi H_2 = K \cdot \exp \left[-E_a / RT \right] \cdot (\sqrt{P_H} - \sqrt{P_L}) \quad \cdot \cdot \cdot (1)$$

ここで、

K : 水素透過係数 (c m³ / c m² · mm)

P_H , P_L : それぞれ水素についての上流側分圧、下流側分圧(atm)

E_a : 拡散に対する活性化エネルギー (= 2 5 5 0 c a l / m o l)

R : 気体定数 (= 1 . 9 8 7 c a l / m o l · k)

T : 絶対温度 (K)

[0036] Here, operating temperature is made into 120 degrees C (=393K), and a downstream hydrogen partial pressure is temporarily set to PL**0atm. Moreover, the Pd-Ag alloy film is adopted as a palladium system metal membrane. Since the thickness and hydrogen permeation multiplier are in inverse proportion, by adjusting thickness, the hydrogen permeation multiplier K can be set as a predetermined value, and the value of K=200-300 can be realized comparatively easily. Upstream hydrogen partial pressure PH which obtains hydrogen flux phiH2 = 1.37cm3 / cm2, and mm from the above-mentioned formula (1) It will be set to PH2=0.0143-0.0322atm if it asks.

[0037] Therefore, when operating the total pressure of hydrogen content fuel gas by 2atm(s), 0.7-1.6-mol % order ***** of the hydrogen concentration in this fuel gas will be good.

[0038] However, in fact, although a larger value than an above-mentioned upstream partial pressure or the value of upstream hydrogen concentration is needed since gas constituents other than that a downstream hydrogen partial pressure is not zero and hydrogen are resisting to diffusion of hydrogen in the gas laminar film formed in the upstream and the downstream of the palladium charge metal membrane concerned, the example which rounded and made the formation conditions of a fuel cell as an experiment is shown below by making an above-mentioned condition value into a standard.

[0039] (Example 1) the example concerning the configuration of the fuel cell which showed this example to drawing 1 -- it is -- as the palladium system alloy film 14 -- the Pa-Ag alloy film -- using -- structure and an operating condition -- and the result of the acquired generation-of-electrical-energy property is shown below.

[0040] Although the hydrogen content gas and oxygen content gas which the fuel cell was made to energize were seen from the cell engine performance and it was superfluous, it turned out that it can generate electricity with the cell configuration proposed by this

invention.

[0041]

(1) Structure conditions of a cell Effective generation-of-electrical-energy area of a cell: 5cmx5cm Electrolyte membrane (quality of the material) : perfluoro sulfonic acid type ion exchange membrane (film thickness) : 125 micrometers (ion exchange capacity Ae) : 1.1 meg/g-resin Catalyst bed (quality of the material) : Pt support carbon particle layer (a hydrogen pole side, oxygen pole side) : 0.12mm (Film thickness) : 1.5 mg/cm² (The amount of Pt support) Hydrogen separation metal membrane (quality of the material) : Pd and Ag alloy film : 25wt% (Ag content) (Film thickness) : [About 10 micrometers] Oxygen electrode (quality of the material) : The sheet made from porosity carbon : About 0.4mm (Thickness) Gas separator (quality of the material) : SUS316L : A width [of 0.4mm] x depth [of 0.5mm] x pitch 1mm (2) operating condition (The shape of a quirk) Temperature : 100 degrees C Pressure: Ordinary pressure Hydrogen content gas (presentation): H₂ : 30-mol %, and H₂O:30-mol %, N₂ : 38.5-mol % and CO:1.5-mol % (flow rate) : 1200 Ncc/min Oxygen content gas (presentation): Humidification air (O₂:19%, N₂:71%, H₂O:10%) : (Flow rate) 1500 Ncc/min (3) generation-of-electrical-energy engine performance Electrical potential difference: 0.7V Current density: 0.08 A/cm² [0042] (Example 2) Next, the example concerning the configuration of the fuel cell shown in drawing 2 is explained. In this example, it has joined to the direct electrolyte membrane 11, using the Pd-Ag alloy film as palladium system alloy film 14. The result of this structure and operating condition, and the generation-of-electrical-energy property which could reach is shown below.

[0043] Although the hydrogen content gas and oxygen content gas which the fuel cell was made to energize were seen from the cell engine performance and concentration distribution had become the amount of overage so that might not be formed in a gas side within a cell, it turned out that it can generate electricity with the cell configuration proposed by this invention.

[0044]

(1) Structure conditions of a cell Effective generation-of-electrical-energy area of a cell: 5cmx5cm Electrolyte membrane (quality of the material) : perfluoro sulfonic acid type ion exchange membrane (film thickness) : 125 micrometers (ion exchange capacity Ae) : 1.1 meg/g-resin Catalyst bed (quality of the material) : Pt support carbon particle layer (however, only oxygen pole side) : 0.12mm (Film thickness) : 1.5 mg/cm² (The amount of Pt support) Hydrogen separation metal membrane (quality of the material) : Pd and Ag alloy film : 25wt% (Ag content) (Film thickness) : [About 10 micrometers] Oxygen electrode (quality of the material) : The sheet made from porosity carbon : About 0.4mm (Thickness) Gas separator (quality of the material) : SUS316L : A width [of 0.4mm] x depth [of 0.5mm] x pitch 1mm (2) operating condition (The shape of a quirk) Temperature : 101 degrees C Pressure: Ordinary pressure Hydrogen content gas (presentation): H₂ : 20-mol %, and H₂O:30-mol %, N₂ : 48.5-mol % and CO:1.5-mol % (flow rate) : 1240 Ncc/min Oxygen content gas (presentation): Humidification air (O₂:19%, N₂:71%, H₂O:10%) : (Flow rate) 1550 Ncc/min (3) generation-of-electrical-energy engine performance Electrical potential difference: 0.71V Current density: 0.05 A/cm² [0045]

[Effect of the Invention] As mentioned above, since the palladium system metal membrane was used as a hydrogen pole according to the fuel cell concerning this invention as stated with the example, the effectiveness which only hydrogen can be penetrated alternatively and shows it below is done so.

- 1) In order to obtain high grade hydrogen like a conventional method, it becomes unnecessary to refine hydrogen, and the whole system is simplified and miniaturized by the deoxo method or membrane-separation method for burning alternatively CO which remains further after CO water gas shift reaction with a catalyst (CO→CO₂), the adsorption purification method, etc.
- 2) The configuration of a fuel cell does not become complicated especially as compared with a conventional method.
- 3) Moreover, in joining a palladium system metal membrane to a direct electrolyte membrane, a catalyst bed becomes unnecessary and structure simplifies.
- 4) So, it can contribute to energy saving and saving resources according to the effectiveness of the above 1-3.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the decomposition perspective view of the gas separator concerning one example.

[Drawing 2] It is the explanatory view showing the components structure of the separator of drawing 1.

[Drawing 3] It is the graph which shows the cell performance curve of a test result.

[Drawing 4] It is the block diagram showing a solid-state polyelectrolyte film fuel cell.

[Description of Notations]

- 11 Electrolyte Membrane
- 12 Catalyst Bed for Hydrogen Dissociation
- 13 Catalyst Bed for Hydro-Acid-izing
- 14 Palladium System Metal Membrane
- 15 Negative-Electrode Side Gas Separator
- 16 Oxygen Electrode
- 17 Positive-Electrode Side Gas Separator
- 18 Hydrogen Content Fuel Gas
- 19 Fuel Gas Passage
- 20 23 Stream
- 21 Oxygen Content Gas
- 22 Oxygen Content Gas Passageway
- 24a Proton H⁺
- 24b Proton H⁺ Flow
- 25 O₂ Flow
- 26a-26c Electron e⁻ Flow
- 27 Electronic Load Resistance

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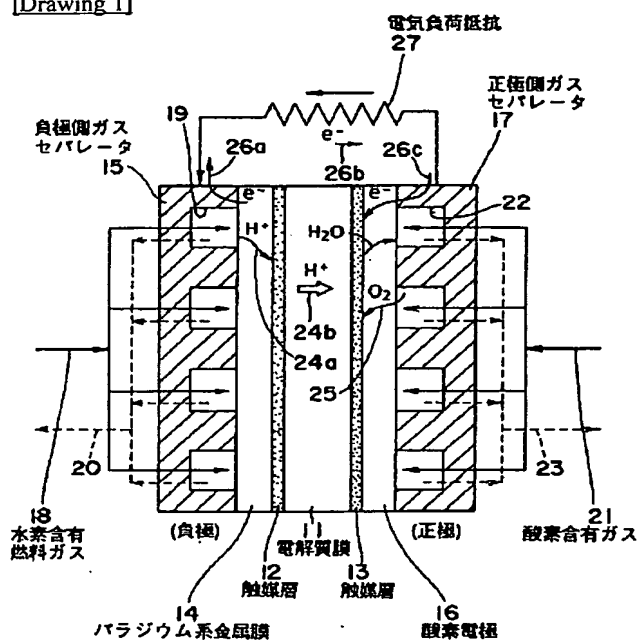
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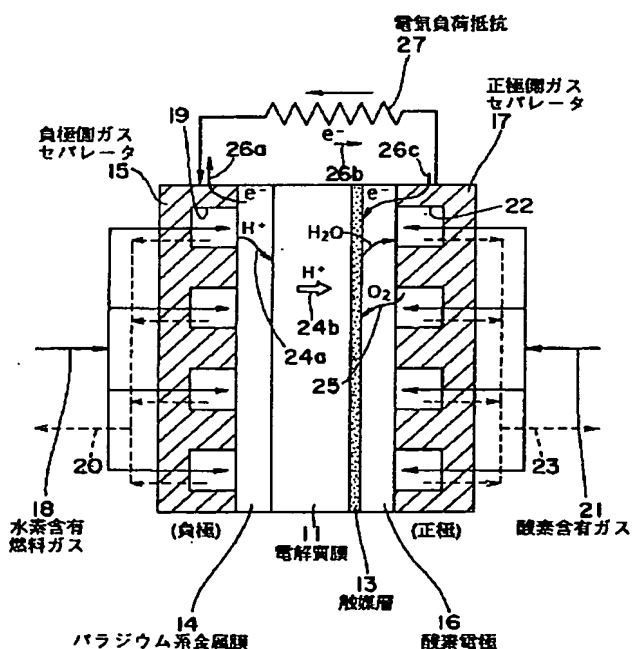
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DRAWINGS

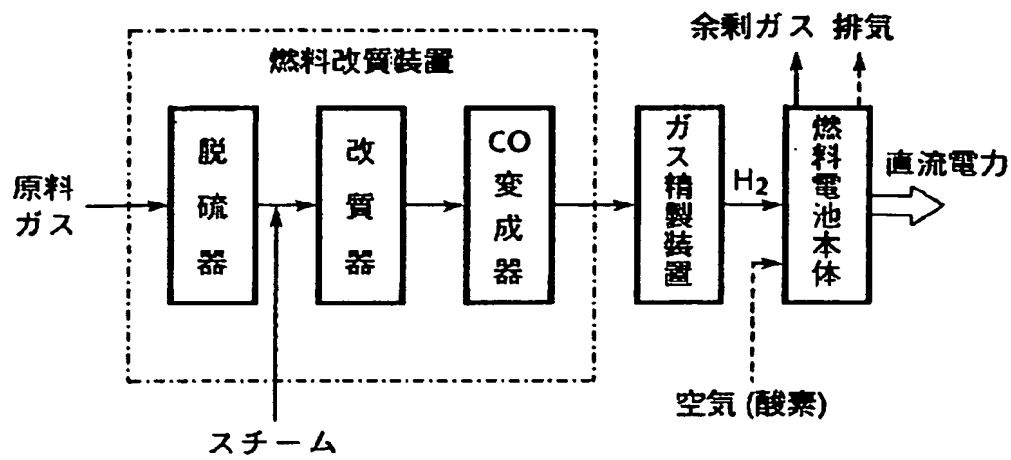
[Drawing 1]



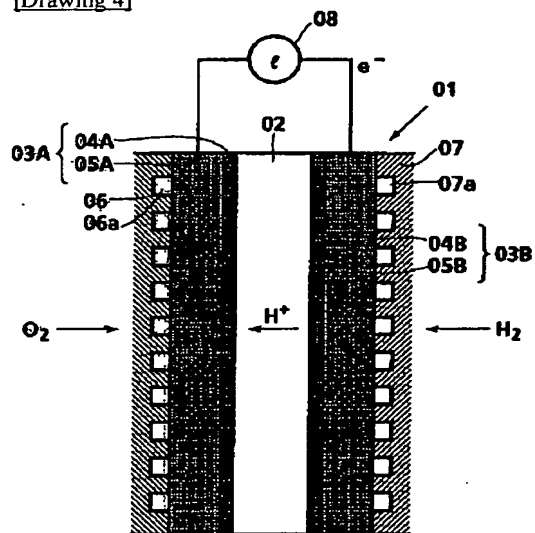
[Drawing 2]



[Drawing 3]



[Drawing 4]



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 WRITTEN AMENDMENT

----- [a procedure revision]

[Filing Date] June 3, Heisei 4

[Procedure amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] Claim 1

[Method of Amendment] Modification

[Proposed Amendment]

[Claim 1] The fuel cell characterized by making hydrogen penetrate preferentially out of the gas which comes to arrange the hydrogen demarcation membrane which makes hydrogen penetrate alternatively to the hydrogen pole side of the electrolyte layer of a proton conduction type in the fuel cell which operates considering the gas containing hydrogen as a fuel, and touches a hydrogen pole through the hydrogen demarcation membrane concerned, and generating electricity by transmitting to said electrolyte layer.

[Procedure amendment 2]

[Document to be Amended] Specification

[Item(s) to be Amended] 0014

[Method of Amendment] Modification

[Proposed Amendment]

[0014]

[Means for Solving the Problem] The configuration of the fuel cell concerning this invention which attains said purpose is characterized by to make hydrogen penetrate preferentially out of the gas which comes to arrange the hydrogen demarcation membrane which makes hydrogen penetrate alternatively to the hydrogen pole side of the electrolyte layer of a proton conduction type, and touches a hydrogen pole through the hydrogen demarcation membrane concerned, and to generate electricity by transmitting to said electrolyte layer in the fuel cell which operates considering the gas containing hydrogen as a fuel.

[Procedure amendment 3]

[Document to be Amended] Specification

[Item(s) to be Amended] 0020

[Method of Amendment] Modification

[Proposed Amendment]

[0020] About passage of the hydrogen in these palladium system metal membranes, many researches are made after discovery of Graham, and the setup of the transparency device is as follows.

- (1) A hydrogen content child sticks to the front face of the film by the side of raw gas.
- (2) Dissociate to a hydrogen atom, with an adsorption hydrogen content child adsorbing.
- (3) An adatom ionizes, separate into a proton and an electron and award an electron to a metal grid.
- (4) It is spread in the opposite side (purification hydrogen side) from a membranous raw gas side in the state of a proton.
- (5) A proton receives an electron from a metal grid in the opposite side, and the atom of the letter of adsorption generates.
- (6) Association of two adsorption hydrogen atoms generates an adsorption hydrogen content child.
- (7) Carry out desorption of the hydrogen content child from a film surface.

Only the hydrogen which carries out a dissociative adsorption and can be in a proton condition by the above-mentioned step can carry out diffuse transmission of the inside of the film.

[Procedure amendment 4]

[Document to be Amended] Specification

[Item(s) to be Amended] 0034

[Method of Amendment] Modification

[Proposed Amendment]

[0034]

[Example] Hereafter, based on the following examples, it explains that the fuel cell by this invention is effective. When an electrical-potential-difference x current characteristic (IV property) operates a cell by 0.15 W/cm² by 0.75Vx0.2 A/cm², i.e., power flux density, it asks for the flux of the hydrogen which flows a cell. Potential efficiency of a cell is made into 64%, and since the hydrogen initial complements of per 1 W are about 0.025 mols / h-w, the hydrogen flux phiH₂ at the time of power-flux-density 0.15 W/cm² serves as mol (0.15 (0.025)) / cm², and h= 1.37cm³/cm² and min. Below, the conditions of the palladium system metal membrane for obtaining the aforementioned hydrogen flux are examined. The hydrogen flux phiH₂ which lets the palladium system metal membrane concerned pass is given by the formula shown in following "number 1."

[Procedure amendment 5]

[Document to be Amended] Specification

[Item(s) to be Amended] 0035

[Method of Amendment] Modification

[Proposed Amendment]

[0035]

[Equation 1]

$$\phi H_2 = K \cdot \exp \left[-E_a / RT \right] \cdot (\sqrt{P_H} - \sqrt{P_L}) \quad \cdot \cdot \cdot ($$

ここで、

K : 水素透過係数 ($\text{cm}^3 / \text{cm}^2 \cdot \text{min}$)

P_H , P_L : それぞれ水素についての上流側分圧、下流側

E_a : 拡散に対する活性化エネルギー ($= 2550 \text{ cal}$,

R : 気体定数 ($= 1.987 \text{ cal} / \text{mol} \cdot \text{K}$)

T : 絶対温度 (K)

[Procedure amendment 6]

[Document to be Amended] Specification

[Item(s) to be Amended] 0036

[Method of Amendment] Modification

[Proposed Amendment]

[0036] Here, operating temperature is made into 120 degrees C (=393K), and a downstream hydrogen partial pressure is temporarily set to $P_L = 0 \text{ atm}$. Moreover, the Pd-Ag alloy film is adopted as a palladium system metal membrane. Since the thickness and hydrogen permeation multiplier are in inverse proportion, by adjusting thickness, the hydrogen permeation multiplier K can be set as a predetermined value, and the value of $K=200-300$ can be realized comparatively easily. It will be set to $P_H=0.0143-0.0322 \text{ atm}$ if it asks for the upstream hydrogen partial pressure P_H which obtains hydrogen flux $\phi H_2 = 1.37 \text{ cm}^3 / \text{cm}^2$ and min from the above-mentioned formula (1).

[Procedure amendment 7]

[Document to be Amended] Specification

[Item(s) to be Amended] 0040

[Method of Amendment] Modification

[Proposed Amendment]

[0040] Although the hydrogen content gas and oxygen content gas which circulated the fuel cell were seen from the cell engine performance and it was superfluous, it turned out that it can generate electricity with the cell configuration proposed by this invention.

[Procedure amendment 8]

[Document to be Amended] Specification

[Item(s) to be Amended] 0041

[Method of Amendment] Modification

[Proposed Amendment]

[0041]

(1) The structure conditions of a cell

Effective generation-of-electrical-energy area of a cell: $5 \text{ cm} \times 5 \text{ cm}$

Electrolyte membrane (quality of the material) : perfluoro sulfonic acid type ion exchange membrane

: (Film thickness) 125 micrometers

(Ion exchange capacity A_e) : 1.1 meq/g-resin

Catalyst bed (quality of the material) : Pt support carbon particle layer (a hydrogen pole side, oxygen pole side)

: (Film thickness) 0.12mm

(The amount of Pt support) : 1.5 mg/cm²

Hydrogen separation metal membrane (quality of the material) : Pd and Ag alloy film

(Ag content) : 25wt%

(Film thickness) : about 10 micrometers

Oxygen electrode (quality of the material): The sheet made from porosity carbon

: (Thickness) About 0.4mm

Gas separator (quality of the material): SUS316L

: (The shape of a quirk) Width [of 0.4mm] x depth [of 0.5mm] x pitch 1mm

(2) Operating condition

Temperature: 100 degrees C

Pressure: Ordinary pressure

Hydrogen content gas (presentation): H₂:30-mol %, and H₂O:30-mol %, 2:38.5 mol % and CO:1.5-mol % of N

(Flow rate) :1200 Ncc/min

Oxygen content gas (presentation): Humidification air (O₂:19% and N₂:71%) H₂O:10%)

(Flow rate) :1500 Ncc/min

(3) Generation-of-electrical-energy engine performance

Electrical potential difference: 0.7V

Current density: 0.08 A/cm²

[Filing Date] June 3, Heisei 4

[Procedure amendment 9]

[Document to be Amended] Specification

[Item(s) to be Amended] 0042

[Method of Amendment] Modification

[Proposed Amendment]

[0042] (Example 2) Next, the example concerning the configuration of the fuel cell shown in drawing 2 is explained. In this example, it has joined to the direct electrolyte membrane 11, using the Pd-Ag alloy film as palladium system alloy film 14. The result of this structure and operating condition, and the generation-of-electrical-energy property which could reach is shown below.

[Procedure amendment 10]

[Document to be Amended] Specification

[Item(s) to be Amended] 0043

[Method of Amendment] Modification

[Proposed Amendment]

[0043] Although the hydrogen content gas and oxygen content gas which circulated the fuel cell were seen from the cell engine performance and concentration distribution had become the amount of overage so that might not be formed in a gas side within a cell, it turned out that it can generate electricity with the cell configuration proposed by this invention.

[Procedure amendment 11]

[Document to be Amended] Specification

[Item(s) to be Amended] 0044

[Method of Amendment] Modification

[Proposed Amendment]

[0044]

(1) The structure conditions of a cell

Effective generation-of-electrical-energy area of a cell: 5cmx5cm

Electrolyte membrane (quality of the material) : perfluoro sulfonic acid type ion exchange membrane

: (Film thickness) 125 micrometers

(Ion exchange capacity Ae) :1.1 meg/g-resin

Catalyst bed (quality of the material) :Pt support carbon particle layer (however, only oxygen pole side)

: (Film thickness) 0.12mm

(The amount of Pt support) :1.5 mg/cm²

Hydrogen separation metal membrane (quality of the material) :Pd and Ag alloy film

(Ag content) :25wt%

(Film thickness) : about 10 micrometers

Oxygen electrode (quality of the material): The sheet made from porosity carbon

: (Thickness) About 0.4mm

Gas separator (quality of the material): SUS316L

: (The shape of a quirk) Width [of 0.4mm] x depth [of 0.5mm] x pitch 1mm

(2) Operating condition

Temperature: 101 degrees C

Pressure: Ordinary pressure

Hydrogen content gas (presentation): H₂:20-mol %, and H₂O:30-mol %, 2:48.5 mol % and CO:1.5-mol % of N

(Flow rate) :1240 Ncc/min

Oxygen content gas (presentation): Humidification air (O₂:19% and N₂:71%)

H₂O:10%)

(Flow rate) :1550 Ncc/min

(3) Generation-of-electrical-energy engine performance

Electrical potential difference: 0.71V

Current density: 0.05 A/cm²

[Procedure amendment 12]

[Document to be Amended] Specification

[Item(s) to be Amended] Easy explanation of a drawing

[Method of Amendment] Modification

[Proposed Amendment]

[Brief Description of the Drawings]

[Drawing 1] It is the block diagram of the fuel cell concerning one example of this invention.

[Drawing 2] It is the block diagram of the fuel cell concerning one another example of this invention.

[Drawing 3] It is drawing showing the outline of the fuel cell system by the conventional technique.

[Drawing 4] It is the block diagram showing the conventional solid-state polyelectrolyte film fuel cell.

[Description of Notations]

11 Electrolyte Membrane

12 Catalyst Bed for Hydrogen Dissociation

13 Catalyst Bed for Hydro-Acid-izing

14 Palladium System Metal Membrane
15 Negative-Electrode Side Gas Separator
16 Oxygen Electrode
17 Positive-Electrode Side Gas Separator
18 Hydrogen Content Fuel Gas
19 Fuel Gas Passage
20 23 Stream
21 Oxygen Content Gas
22 Oxygen Content Gas Passageway
24a Proton H⁺
24b Flow of proton H⁺
25 Flow of O₂
26a-26c Flow of electronic e⁻
27 Electronic Load Resistance

[Translation done.]

EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

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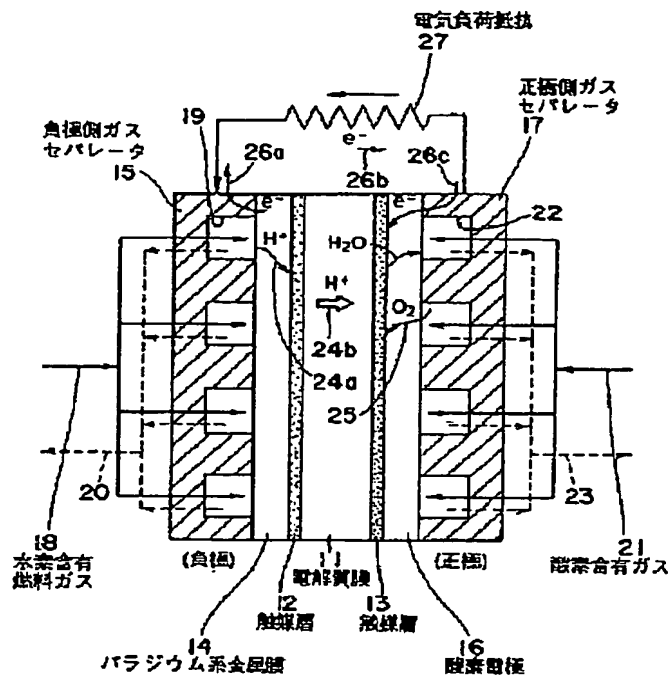
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APPLICANT : MITSUBISHI HEAVY IND LTD;

INVENTOR : UCHIDA TOSHIYUKI;

INT.CL. : H01M 8/02 H01M 8/10

TITLE : FUEL BATTERY



ABSTRACT : PURPOSE: To provide a fuel battery to which a reformed gas can be directly supplied.

CONSTITUTION: In a fuel battery in which a gas 18 containing hydrogen is used as a fuel, a palladium series metal film 14 is provided as a hydrogen separation film of selectively transmitting hydrogen into the hydrogen pole side of a proton conduction type electrolyte layer 11. Hydrogen is preferentially transmitted from the gas touching the hydrogen pole through the palladium series metal film and transferred to the foregoing electrolyte layer to generate an electric power, so that a reformed gas can be supplied as a fuel direction to the battery without the gas containing hydrogen obtained by particularly reforming the fuel being refined with high purity in advance.

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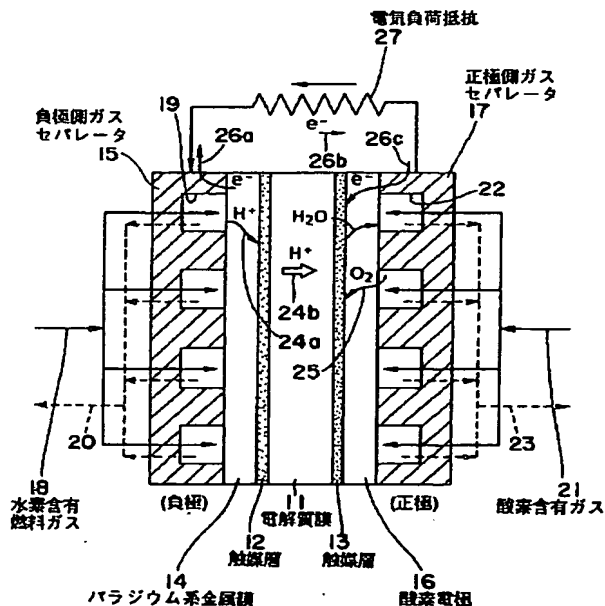
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(54)【発明の名称】 燃料電池

(57)【要約】

【目的】 改質ガスを直接当該燃料電池に供給できる燃料電池を提供することを目的とする。

【構成】 水素含有ガス18を燃料として作動する燃料電池において、プロトン伝導型の電解質層11の水素極側に水素を選択的に透過させる水素分離膜としてパラジウム系金属膜14を配設してなり、当該パラジウム系金属膜14を介して水素極に接するガス中から水素を優先的に透過させ、前記電解質層11に伝達して発電を行うもので、特に当該燃料を改質して得られる水素含有ガスをあらかじめ高純度に精製することなく直接改質ガスを燃料として当該電池の水素極に供給できる。



【特許請求の範囲】

【請求項1】 水素を含有するガスを燃料として作動する燃料電池において、プロント伝導型の電解質層の水素極側に水素を選択的に透過させる水素分離膜を配設してなり、当該水素分離膜を介して水素極に接するガス中から水素を優先的に透過させ、前記電解質層に伝達して発電を行うことを特徴とする燃料電池。

【発明の詳細な説明】

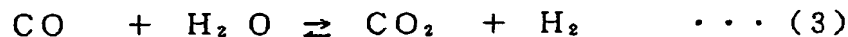
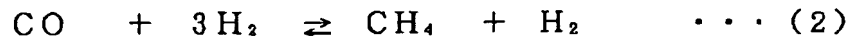
【0001】

【産業上の利用分野】本発明は、メタン等の炭化水素又は、メタノール等のアルコールを燃料とする燃料電池に関し、特に当該燃料を改質して得られる水素含有ガスをあらかじめ高純度に精製することなく直接に改質ガスを燃料として当該電池の水素極に供給し得るように工夫したものである。

【0002】

【従来の技術】燃料電池は、資源の枯渇問題を有する化石燃料を使う必要がない上、騒音をほとんど発生せず、エネルギーの回収効率も他のエネルギー機関と較べて非常に高くできる等の優れた特徴を持っているため、例えばビルディング単位や工場単位の比較的小型の発電プラントとして利用されている。近年、この燃料電池を車載用の内燃機関に代えて作動するモータの電源として利用し、このモータにより車両等を駆動することが考えられている。この場合に重要なことは、反応によって生成する物質をできるだけ再利用することは当然のこととして、車載用であることから明らかなように、余り大きな出力は必要でないものの、全ての付帯設備と共に可能な限り小型であることが望ましく、このような点からイオン交換膜を使用する燃料電池、特に固体高分子電解質膜燃料電池が注目されている。

【0003】ここで、一例として固体高分子電解質膜燃料電池本体の基本構造を図4を参照しながら説明する。同図に示すように、電池本体01は固体高分子電解質膜02の両側にガス拡散電極03A、03Bが接合される



【0007】上記メタン等の炭化水素の改質反応は、熱力学的平衡の観点から、温度が高く、圧力が低くかつ水蒸気比が多いほど、 $\text{H}_2 + \text{CO}$ の濃度が高くなる方に反応が進行する。

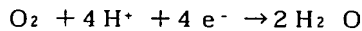
【0008】その結果、改質器の出口ガスは、 H_2 のほか CH_4 、 H_2O 、 CO 、 CO_2 のガスが含まれるが、一般に燐酸型や固体高分子電解質膜型の燃料電池では、 CO が触媒毒となるため、改質器からの改質ガスは直接燃料電池用の燃料ガスとしては使用できない。

【0009】そこで、改質ガスを CO 変成器に送入し

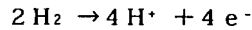
ことにより構成されている。そしてこの接合体は、固体高分子電解質膜02の両側にガス拡散電極03A、03Bを合せた後、ホットプレス等することにより製造される。また、ガス拡散電極03A、03Bはそれぞれ反応膜04A、04B及びガス拡散膜05A、05Bが接合されたものであり、電解質膜02とは反応膜04A、04Bの表面が接触している。したがって、電池反応は主に電解質膜02と反応膜04A、04Bとの間の接触面で起こる。また、上記ガス拡散電極03Aの表面には、酸素供給溝06aを有するガスセパレータが、また他方のガス拡散電極03Bの表面には水素供給溝07aを有するガスセパレータ07がそれぞれ接合されており、酸素極と水素極を構成している。

【0004】そして、酸素供給溝06a及び水素供給溝07aは酸素及び水素をそれぞれ供給すると、酸素、水素は、各々のガス拡散膜05A、05Bを介して反応膜04A、04B側へ供給され、各反応膜04A、04Bと電解質膜02との界面で次のような反応が起こる。

反応膜04Aの界面：



反応膜04Bの界面：



ここで、 4H^+ は電解質膜02を通過して水素極から酸素極へ流れるが、 4e^- は負荷08を通過して水素極から酸素極へ流れることになり、電気エネルギーが得られる。

【0005】ところで、炭化水素又はアルコールを原料として用いた場合、燃料電池を稼働して電力を得る従来の方法としては、図3に示すようなものがある。同図において、原料ガスをまず脱硫したのち、所定の割合でスチームを混合して改質器に送入すると改質触媒の存在下に次のような水蒸気改質反応が進行する。すなわち、メタンの例で示すと、下記「化1」に示す反応式(1)～(3)の反応が進行する。

【0006】

【化1】

て、触媒存在下に前述の反応(3)により CO を H_2 に転換し、 CO 濃度を0.5～1%程度に軽減することが行われる。さらに CO 濃度を低下させる必要がある場合には、 CO 変成後のガスをさらにガス精製装置にかけ、例えば CO を10ppm以下になるまで純度を上げることが行われる。この時のガス精製法としては、深冷分離法、吸着分離法、パラジウム触媒によるデオキシソ法、湿式吸収精製法、パラジウム系合金膜による拡散法などの手段がある。

【0010】このようにして得られる高純度の水素を含

有する（特に、CO濃度を低減した）ガスを燃料電池の水素極に供給し、他方、酸素極には空気もしくは酸素ガスを供給することで、水素の燃焼熱を直流電力に変換させている。

【0011】

【発明が解決しようとする課題】前述したような従来技術では、燃料電池の特に電極部触媒反応層を被毒させないように特にCOの濃度低減に複雑な処理工程（図3参照）を余儀なくされている。

【0012】すなわち、水蒸気改質反応以降においては以下のような欠点がある。

- 1) CO変成器を必要とする。
- 2) 場合によっては、さらに高度精製装置を必要とする。
- 3) その結果、装置費、運転費とも高価となり経済性を悪くしている。

【0013】本発明は上記問題に鑑み、改質ガスを直接当該燃料電池に供給できる燃料電池を提供することを目的とする。

【0014】

【課題を解決するための手段】前記目的を達成する本発明に係る燃料電池の構成は、水素を含有するガスを燃料として作動する燃料電池において、プロトン伝導型の電解質層の水素極側に水素を選択的に透過させる水素分離膜を配設してなり、当該水素分離膜を介して水素極に接するガス中から水素を優先的に透過させ、前記電解質層に伝達して発電を行うことを特徴とする。

【0015】以下、本発明に係る燃料電池の内容を詳細に説明する。

【0016】図1には本発明に係る燃料電池の概略を示す構成図である。同図に示すように、電解質膜11の一方の側面に水素解離用の触媒層12を設けると共に他方の側面に水素酸化用の触媒層13を設けている。また、一方の水素解離用の触媒層12の側面には水素電極を兼ねる水素分離膜としてのパラジウム系金属膜14並びに負極側ガスセパレータ15を順次重ね合わせている。他方の水素酸化用の触媒層13の側面にも多孔質性の酸素電極16並びに正極側ガスセパレータ17を順次重ね合わせている。

【0017】そして、改質ガスとしての水素含有燃料ガス18は上記負極側ガスセパレータ15に形成された燃料ガス流路19に供給され、一部水素が消費された後、ストリーム20として系外に排出される。他方、空気などの酸素含有ガス21は、反対側の正極側ガスセパレータ17に形成された酸素含有ガス流路22に供給され、一部酸素が消費された後、ストリーム23として系外に排出される。

【0018】ここで上記水素電極を兼ねる水素分離膜としてのパラジウム系金属膜14は、水素含有燃料ガス1
水素解離用の触媒層12において、

8中の水素のみを選択的に透過させる能力を有するものであり、上記水素含有燃料ガス18の水素を当該パラジウム系金属膜14中を透過してプロトン伝導型の電解質膜11に導くようにしている。

【0019】この水素を選択的に透過させるパラジウム系金属膜14としては、例えばPd単味膜、Pd-Ag合金膜、Pd-Y合金膜、Pd-Ag-Au-Ru合金膜などを挙げることができる。

【0020】これらのパラジウム系金属膜における水素の通過については、Grahamの発見以降多くの研究がなされており、その透過機構の設定は、次のとおりである。

- (1) 処理ガス側の膜の表面に水素分子が吸着する。
- (2) 吸着水素分子が吸着したまま水素原子に解離する。
- (3) 吸着原子が電離しプロトンと電子に分離し、電子を金属格子に授与する。
- (4) プロトンの状態で膜の処理ガス側から反対側（精製水素側）に拡散する。
- (5) 反対側でプロトンが金属格子から電子を受容し吸着状の原子が生成する。
- (6) 吸着水素原子2個の結合により、吸着水素分子を生成する。
- (7) 膜面から水素分子の脱着する。

上述のステップにより、解離吸着してプロトン状態になりうる水素のみが、膜中を拡散透過できることとなる。

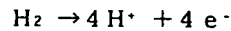
【0021】次に、上記パラジウム系金属膜14を水素極とした燃料電池の燃料として供給される水素と酸との挙動と発生する電力との関係について、以下に説明する。

【0022】まず、水素は負極側の燃料ガス流路19側から前記パラジウム系金属膜14に浸入し、当膜の選択的水素透過機能により、プロトン H^+ 24a状態で当該パラジウム系金属膜14の他端に移動したのち、水素分子の状態で水素解離用の触媒層12に拡散する。次に当該触媒層12の触媒作用で水素分子は解離してプロトン H^+ と電子 e^- とを生成する。さらに、当該プロトン H^+ は、電解質膜11を拡散するプロトン H^+ の流れ24bとなって、水素酸化用の触媒層13に到達し、正極側の酸素含有ガス流路22側から多孔性の酸素電極15の中を拡散してくる O_2 の流れ25ならびに、外部電気回路を通じて流入する。電子 e^- の流れ26cと合流して反応し、 H_2O を生成する。当該 H_2O は酸素電極15の中を O_2 の流れ25とは逆向きに拡散して正極側酸素含有ガス流路20に到達し排出される。

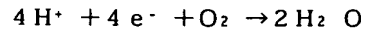
【0023】すなわち、電極部での反応をまとめると、下記「化2」に示すようになる。

【0024】

【化2】



水素酸化用の触媒層13において、



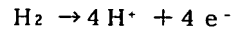
【0025】上記反応(4)で生成する電子 e^- は、電子 e^- の流れ26a、26b、26cとなって反対極側に移動し反応(5)に寄与する。このとき、電子 e^- の流れが電気負荷抵抗27を通過する際、電力として出力されることになる。

【0026】上記説明においては、負極側に設けた水素を選択的に透過させる水素分離膜としてのパラジウム系金属膜14は、図1に示すように電解質膜11の側面に設けた水素分離膜用の触媒層12の一側面に設けているが、この水素分離膜用の触媒層12を用いないで構成してなる燃料電池の説明を図2を参照して説明する。

【0027】図2に示す燃料電池の構成は、図1に示す燃料電池と比べると、電解質膜11の側面にパラジウム系金属膜14を直接接合し、水素分離膜用の触媒13を不用としている点が異なるものであるが、その他の構成は図1に示す燃料電池の構成と同様としている。よって、重複する部材については、重複した番号を付してそ

【0028】次に、上記パラジウム系金属膜14を水素極とし且つ直接電解質膜11と接合してなる燃料電池の

水素を選択的に透過するパラジウム系金属膜14の表面(水素極側)において、



水素酸化用の触媒層13において、



【0032】上記反応(6)で生成する電子 e^- は、電子 e^- の流れ26a、26b、26cとなって反対極側に移動し反応(7)に寄与する。このとき、電子 e^- の流れが電気負荷抵抗27を通過する際、電力として出力されることになる。

【0033】上記、パラジウム系金属膜14は、水素を吸着解離・電離させる作用があり、水素は膜中をプロトン H^+ の状態で移動する。従って、パラジウム系金属膜14と電解質膜11とを直接接合することで、プロトン H^+ の流れをパラジウム系金属膜14から電解質膜11に受け渡すことができる。

【0034】

【実施例】以下、本発明による燃料電池が有効であることを、以下の実施例に基づいて説明する。電圧×電流特

・・・(4)

・・・(5)

燃料として供給される水素と酸との挙動と発生する電力との関係について、以下図2を参照して説明する。

【0029】先ず、水素は負極側の燃料ガス流路19側から前記パラジウム系金属膜14に浸入し、当膜の選択的水素透過機能により、プロトン H^+ 24a状態で当該パラジウム系金属膜14の他端に移動したのち、プロトン H^+ 24aの状態のまま当該電解質膜11の中に進入し、さらに、当該プロトン H^+ は、電解質膜11を拡散するプロトン H^+ の流れ24bとなって、水素酸化用の触媒層13に到達し、正極側の酸素含有ガス流路22側から多孔性の酸素電極15の中を拡散してくる O_2 の流れ25ならびに、外部電気回路を通じて流入する。電子 e^- の流れ26cと合流して反応し、 H_2O を生成する。当該 H_2O は酸素電極15の中を O_2 の流れ25とは逆向きに拡散して正極側酸素含有ガス流路20に到達し排出される。

【0030】すなわち、電極部での反応をまとめると、下記「化3」に示すようになる。

【0031】

【化3】

・・・(6)

・・・(7)

性(IV特性)が $0.75\text{V} \times 0.2\text{A}/\text{cm}^2$ すなわち電力密度で $0.15\text{W}/\text{cm}^2$ にて電池を動作させるとき、電池を流れる水素のフラックスを求めてみる。電池の電圧効率を64%として、1W当りの水素必要量は約 $0.025\text{mol}/\text{h} \cdot \text{w}$ であるから、電力密度 $0.15\text{W}/\text{cm}^2$ のときの水素フラックス ϕ_{H_2} は $(0.025)(0.15)\text{mol}/\text{cm}^2 \cdot \text{h} = 1.37\text{cm}^3/\text{cm}^2 \cdot \text{mm}$ となる。つぎに、前記の水素フラックスを得るためのパラジウム系金属膜の条件を検討してみる。当該パラジウム系金属膜を通しての水素フラックス ϕ_{H_2} は、下記「数1」に示す式で与えられる。

【0035】

【数1】

$$\phi H_2 = K \cdot \exp \left[-E_a / RT \right] \cdot (\sqrt{P_H} - \sqrt{P_L}) \quad \dots (1)$$

ここで、

K : 水素透過係数 ($\text{cm}^3 / \text{cm}^2 \cdot \text{mm}$)

P_H, P_L : それぞれ水素についての上流側分圧、下流側分圧(atm)

E_a : 拡散に対する活性化エネルギー ($= 2550 \text{ cal/mol}$)

R : 気体定数 ($= 1.987 \text{ cal/mol} \cdot \text{K}$)

T : 絶対温度 (K)

【0036】ここで、操作温度を 120°C ($= 393 \text{ K}$)とし、下流側水素分圧は仮に $P_L = 0 \text{ atm}$ とする。また、パラジウム系金属膜として、 $\text{Pd} \cdot \text{Ag}$ 合金膜を採用する。その膜厚と水素透過係数とは反比例するので、膜厚を調整することで、水素透過係数 K を所定値に設定することができ、比較的容易に $K = 200 \sim 300$ の値を実現することができる。上記数式(1)から、水素フラックス $\phi H_2 = 1.37 \text{ cm}^3 / \text{cm}^2 \cdot \text{mm}$ を得る上流側水素分圧 P_H を求めると、 $P_H = 0.0143 \sim 0.0322 \text{ atm}$ となる。

【0037】従って、水素含有燃料ガスの全圧を 2 atm で操作する場合には、同燃料ガス中の水素濃度は $0.7 \sim 1.6$ モル%のオーダーであれば良いこととなる。

【0038】しかし、実際には下流側水素分圧はゼロではないこと、水素以外のガス成分は、当該パラジウム係

金属膜の上流側および下流側に形成されるガス境膜において水素の拡散に対して抵抗となるため、上述の上流側分圧又は上流側水素濃度の値よりも大きい値が必要となるが、上述の条件値を目安として燃料電池の成立条件を繰り込み、試作した実施例を以下に示す。

【0039】(実施例1)本例は、図1に示した燃料電池の構成に係る実施例であり、パラジウム系合金膜14として $\text{Pd} \cdot \text{Ag}$ 合金膜を用い、構造および操作条件と及び得られた発電特性の結果を以下に示す。

【0040】燃料電池に通電させた水素含有ガスおよび酸素含有ガスは、電池性能から見て過剰となっているが、本発明で提案した電池構成で発電できることが判った。

【0041】

(1) 電池の構造条件

セルの有効発電面積 : $5 \text{ cm} \times 5 \text{ cm}$

電解質膜 (材質) : パーフルオロスルホン酸型イオン交換膜

(膜厚さ) : $125 \mu\text{m}$

(イオン交換容量 A_e) : 1.1 meq/g-resin

触媒層 (材質) : Pt担持カーボン粒子層 (水素極側、酸素極側)

(膜厚さ) : 0.12 mm

(Pt担持量) : 1.5 mg/cm^2

水素分離金属膜 (材質) : $\text{Pd} \cdot \text{Ag}$ 合金膜

(Ag含有率) : $25 \text{ wt}\%$

(膜厚さ) : 約 $10 \mu\text{m}$

酸素電極 (材質) : 多孔質カーボン製シート

(厚さ) : 約 0.4 mm

ガスセパレータ (材質) : SUS316L

(溝形状) : 巾 $0.4 \text{ mm} \times$ 深さ $0.5 \text{ mm} \times$ ピッチ 1 mm

(2) 操作条件

温度 : 100°C

圧力 : 常圧

水素含有ガス (組成) : H_2 : $30 \text{ モル}\%$, H_2O : $30 \text{ モル}\%$,

N_2 : $38.5 \text{ モル}\%$, CO : $1.5 \text{ モル}\%$

(流量) : 1200 Ncc/min

酸素含有ガス(組成): 加湿空気 (O_2 : 19%, N_2 : 71%,
 H_2O : 10%)
 (流量): 1500 Ncc/min

(3) 発電性能

電圧: 0.7 V

電流密度: 0.08 A/cm²

【0042】(実施例2) 次に、図2に示した燃料電池の構成に係る実施例を説明する。本実施例では、パラジウム系合金膜14としてPa・Ag合金膜を用い、直接電解質膜11と接合している。この構造および操作条件と及び得られた発電特性の結果を以下に示す。

酸素含有ガスは、電池内でガス側に濃度分布が形成されないように、電池性能から見て過剰供給量となっているが、本発明で提案した電池構成で発電できることが判った。

【0044】

【0043】燃料電池に通電させた水素含有ガスおよび

(1) 電池の構造条件

セルの有効発電面積: 5 cm × 5 cm

電解質膜(材質): パーフルオロスルホン酸型イオン交換膜

(膜厚さ): 125 μm

(イオン交換容量Ae): 1.1 meq/g-resin

触媒層(材質): Pt担持カーボン粒子層(ただし、酸素極側のみ)

(膜厚さ): 0.12 mm

(Pt担持量): 1.5 mg/cm²

水素分離金属膜(材質): Pa・Ag合金膜

(Ag含有率): 25 wt%

(膜厚さ): 約10 μm

酸素電極(材質): 多孔質カーボン製シート

(厚さ): 約0.4 mm

ガスセパレータ(材質): SUS316L

(溝形状): 巾0.4 mm × 深さ0.5 mm × ピッチ1 mm

(2) 操作条件

温度: 101℃

圧力: 常圧

水素含有ガス(組成): H_2 : 20モル%, H_2O : 30モル%,
 N_2 : 48.5モル%, CO : 1.5モル%

(流量): 1240 Ncc/min

酸素含有ガス(組成): 加湿空気 (O_2 : 19%, N_2 : 71%,
 H_2O : 10%)

(流量): 1550 Ncc/min

(3) 発電性能

電圧: 0.71 V

電流密度: 0.05 A/cm²

【0045】

【発明の効果】以上、実施例と共に述べたように本発明に係る燃料電池によれば、パラジウム系金属膜を水素極として用いたので、水素のみを選択的に透過でき下記に示す効果を奏する。

1) 従来法のように高純度水素を得るためにCOシフト反応後さらに残存するCOを触媒で選択的に燃焼($CO \rightarrow CO_2$)させるデオキシ法あるいは膜分離法や吸着精製法などによって水素を精製する必要がなくなり、システム全体が簡素化、コンパクト化される。

2) 燃料電池の構成は、従来法に比較して特に複雑にな

40 ることはない。

3) また、パラジウム系金属膜を直接電解質膜と接合する場合には、触媒層が不要となり、構造が簡素化する。

4) それ故に、上記1)～3)の効果により省エネ・省資源に貢献できる。

【図面の簡単な説明】

【図1】一実施例に係るガスセパレータの分解斜視図である。

【図2】図1のセパレータの部品構造を示す説明図である。

【図3】試験結果の電池性能曲線を示すグラフである。

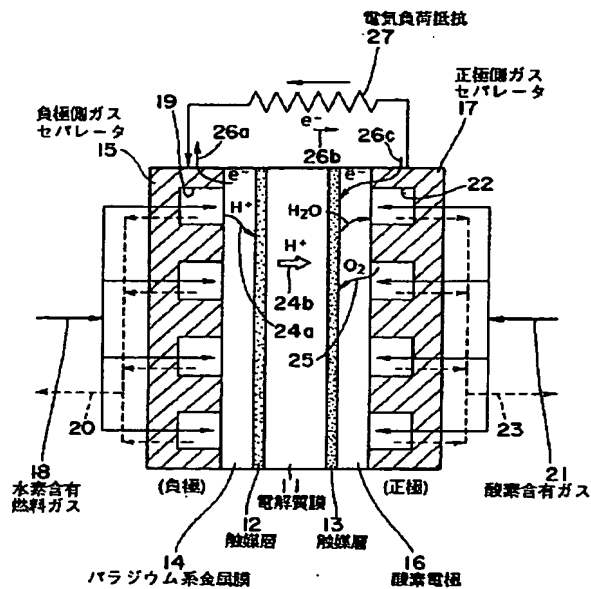
【図4】固体高分子電解質膜燃料電池を示す構成図である。

【符号の説明】

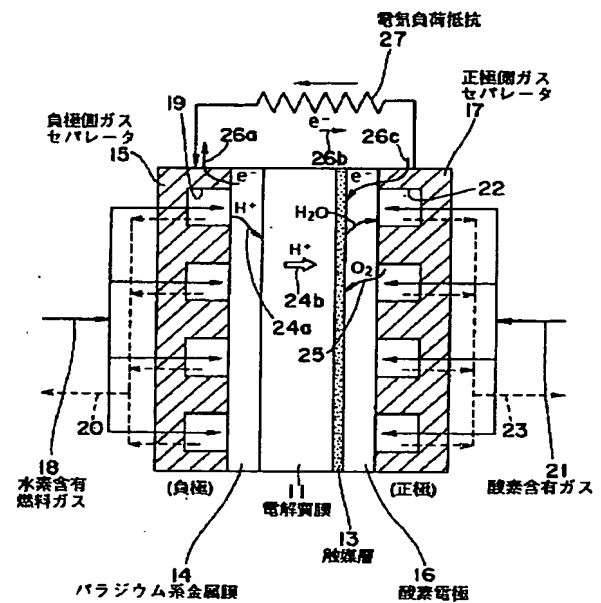
- 1 1 電解質膜
- 1 2 水素解離用の触媒層
- 1 3 水素酸化用の触媒層
- 1 4 パラジウム系金属膜
- 1 5 負極側ガスセパレータ
- 1 6 酸素電極
- 1 7 正極側ガスセパレータ

- 1 8 水素含有燃料ガス
- 1 9 燃料ガス流路
- 2 0, 2 3 ストリーム
- 2 1 酸素含有ガス
- 2 2 酸素含有ガス流路
- 2 4 a プロトン H^+
- 2 4 b プロトン H^+ の流れ
- 2 5 O_2 の流れ
- 2 6 a ~ 2 6 c 電子 e^- の流れ
- 10 2 7 電子負荷抵抗

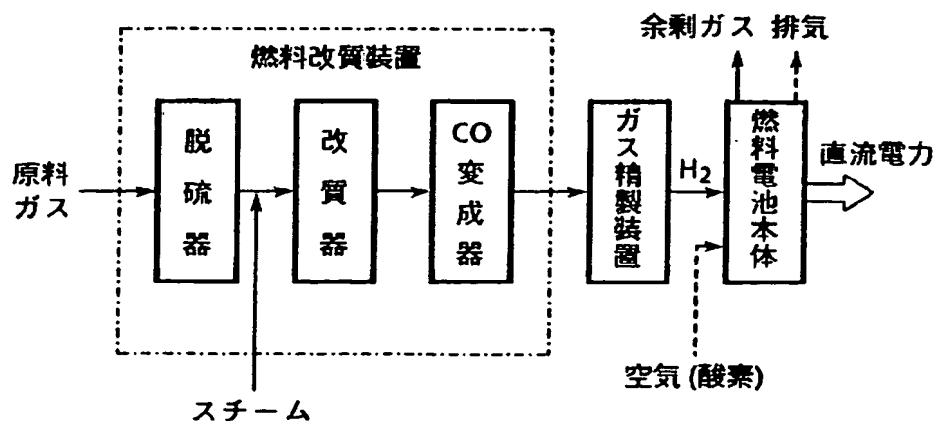
【図1】



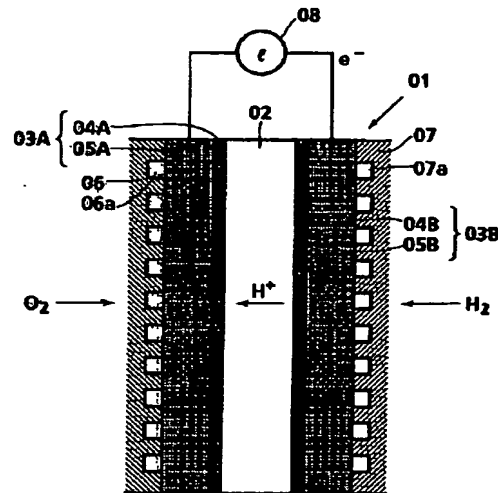
【図2】



【図3】



【図4】



【手続補正書】

【提出日】平成4年6月3日

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】請求項1

【補正方法】変更

【補正内容】

【請求項1】 水素を含有するガスを燃料として作動する燃料電池において、プロトン伝導型の電解質層の水素極側に水素を選択的に透過させる水素分離膜を配設してなり、当該水素分離膜を介して水素極に接するガス中から水素を優先的に透過させ、前記電解質層に伝達して発電を行うことを特徴とする燃料電池。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0014

【補正方法】変更

【補正内容】

【0014】

【課題を解決するための手段】前記目的を達成する本発明に係る燃料電池の構成は、水素を含有するガスを燃料として作動する燃料電池において、プロトン伝導型の電解質層の水素極側に水素を選択的に透過させる水素分離膜を配設してなり、当該水素分離膜を介して水素極に接するガス中から水素を優先的に透過させ、前記電解質層に伝達して発電を行うことを特徴とする。

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0020

【補正方法】変更

【補正内容】

【0020】これらのパラジウム系金属膜における水素の通過については、Grahamの発見以降多くの研究がなされており、その透過機構の設定は、次のとおりである。

- (1) 処理ガス側の膜の表面に水素分子が吸着する。
- (2) 吸着水素分子が吸着したまま水素原子に解離する。
- (3) 吸着原子が電離しプロトンと電子に分離し、電子を金属格子に授与する。
- (4) プロトンの状態で膜の処理ガス側から反対側（精製水素側）に拡散する。
- (5) 反対側でプロトンが金属格子から電子を受容し吸着状の原子が生成する。
- (6) 吸着水素原子2個の結合により、吸着水素分子を生成する。
- (7) 膜面から水素分子を脱着する。

上述のステップにより、解離吸着してプロトン状態になりうる水素のみが、膜中を拡散透過できることとなる。

【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0034

【補正方法】変更

【補正内容】

【0034】

【実施例】以下、本発明による燃料電池が有効であることを、以下の実施例に基づいて説明する。電圧×電流特

性(IV特性)が $0.75V \times 0.2A/cm^2$ すなわち電力密度で $0.15W/cm^2$ にて電池を動作させるとき、電池を流れる水素のフラックスを求めてみる。電池の電圧効率を64%として、1W当りの水素必要量は約 0.025 モル/h・wであるから、電力密度 $0.15W/cm^2$ のときの水素フラックス ϕH_2 は $(0.025)(0.15)$ モル/ $cm^2 \cdot h = 1.37 cm^3/cm^2 \cdot min$ となる。つぎに、前記の水素フラックスを得るためのパラジウム系金属膜の条件を検討してみる。当該パラジウム系金属膜を通しての水素フラックス

$$\phi H_2 = K \cdot \exp[-E_a/RT] \cdot (\sqrt{P_H} - \sqrt{P_L}) \quad \dots (1)$$

ここで、

K : 水素透過係数 ($cm^3/cm^2 \cdot min$)

P_H, P_L : それぞれ水素についての上流側分圧、下流側分圧(atm)

E_a : 拡散に対する活性化エネルギー ($= 2550 cal/mol$)

R : 気体定数 ($= 1.987 cal/mol \cdot K$)

T : 絶対温度 (K)

【手続補正6】

【補正対象書類名】明細書

【補正対象項目名】0036

【補正方法】変更

【補正内容】

【0036】ここで、操作温度を $120^\circ C (= 393 K)$ とし、下流側水素分圧は仮に $P_L \approx 0 atm$ とする。また、パラジウム系金属膜として、Pd・Ag合金膜を採用する。その膜厚と水素透過係数とは反比例するので、膜厚を調整することで、水素透過係数 K を所定値に設定することができ、比較的容易に $K = 200 \sim 300$ の値を実現することができる。上記数式(1)から、水素フラックス $\phi H_2 = 1.37 cm^3/cm^2 \cdot min$ を得る上流側水素分圧 P_H を求めると、 $P_H = 0.0143 \sim 0.0322 atm$ となる。

(1) 電池の構造条件

セルの有効発電面積 : $5 cm \times 5 cm$

電解質膜(材質) : パーフルオロスルホン酸型イオン交換膜

(膜厚さ) : $125 \mu m$

(イオン交換容量 A_e) : $1 meq/g-resin$

触媒層(材質) : Pt担持カーボン粒子層(水素極側、酸素極側)

(膜厚さ) : $0.12 mm$

(Pt担持量) : $1.5 mg/cm^2$

水素分離金属膜(材質) : Pd・Ag合金膜

(Ag含有率) : $25 wt\%$

(膜厚さ) : 約 $10 \mu m$

酸素電極(材質) : 多孔質カーボン製シート

ϕH_2 は、下記「数1」に示す式で与えられる。

【手続補正5】

【補正対象書類名】明細書

【補正対象項目名】0035

【補正方法】変更

【補正内容】

【0035】

【数1】

【手続補正7】

【補正対象書類名】明細書

【補正対象項目名】0040

【補正方法】変更

【補正内容】

【0040】燃料電池に流通させた水素含有ガスおよび酸素含有ガスは、電池性能から見て過剰となっているが、本発明で提案した電池構成で発電できることが判った。

【手続補正8】

【補正対象書類名】明細書

【補正対象項目名】0041

【補正方法】変更

【補正内容】

【0041】

酸素含有ガス（組成）：加湿空気（ O_2 ：19%， N_2 ：71%，
 H_2O ：10%）
（流量）：1550Ncc/min

(3) 発電性能

電圧：0.71V

電流密度：0.05A/cm²

【手続補正12】

【補正対象書類名】明細書

【補正対象項目名】図面の簡単な説明

【補正方法】変更

【補正内容】

【図面の簡単な説明】

【図1】本発明の一実施例に係る燃料電池の構成図である。

【図2】本発明の別の一実施例に係る燃料電池の構成図である。

【図3】従来技術による燃料電池システムの概略を示す図である。

【図4】従来の固体高分子電解質膜燃料電池を示す構成図である。

【符号の説明】

11 電解質膜

12 水素解離用の触媒層

13 水素酸化用の触媒層

14 パラジウム系金属膜

15 負極側ガスセパレータ

16 酸素電極

17 正極側ガスセパレータ

18 水素含有燃料ガス

19 燃料ガス流路

20、23 ストリーム

21 酸素含有ガス

22 酸素含有ガス流路

24a プロトン H^+

24b プロトン H^+ の流れ

25 O_2 の流れ

26a～26c 電子 e^- の流れ

27 電子負荷抵抗

フロントページの続き

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